

# Molecular Scale Devices and Systems Challenges and Perspectives

Call ICT-2009.8.7  
ÅMOL-IT

Françoise Remacle

Theoretical Physical Chemistry

Department of Chemistry, University of Liège, Belgium

Coordinator :

- FET-proactive Nano-ICT project MOLOC (2008-11), call 8.1 on new functionalities.
- FET-Open MOLDYNLOGIC project (2005-07)

# Molecular scale devices and systems

Call ICT-2009.8.7: Four challenges

Devices and systems



- **control at the atomic and molecular scale**
  - positional
  - addressing and reading
  - control of internal states dynamics
    - as in ‘coherent control’
- **interconnection, concatenation**
- **new scalable concepts and architectures**
- **interfacing with the mesoscopic world**

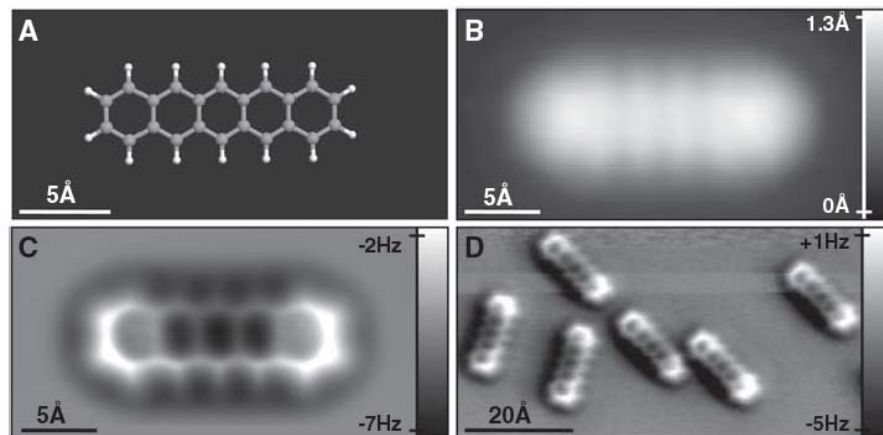
Lessons from MOLDYNLOGIC and MOLOC

# Perspectives on control at the atomic and molecular scale

Control is essential because it allows for reproducibility and scalability

- Difficulty of imaging at the atomic (Angström) scale.

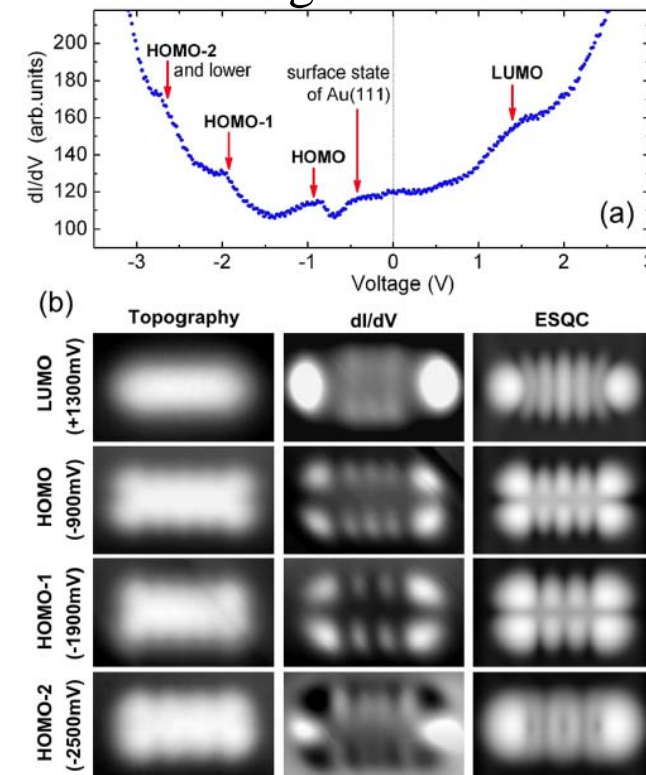
NC-AFM allows to get to an Å resolution



**Fig. 1.** STM and AFM imaging of pentacene on Cu(111). **(A)** Ball-and-stick model of the pentacene molecule. **(B)** Constant-current STM and **(C and D)** constant-height AFM images of pentacene acquired with a CO-modified tip. Imaging parameters are as follows: **(B)** set point  $I = 110$  pA,  $V = 170$  mV; **(C)** tip height  $z = -0.1$  Å [with respect to the STM set point above Cu(111)], oscillation amplitude  $A = 0.2$  Å; and **(D)**  $z = 0.0$  Å,  $A = 0.8$  Å. The asymmetry in the molecular imaging in **(D)** (showing a "shadow" only on the left side of the molecules) is probably caused by asymmetric adsorption geometry of the CO molecule at the tip apex.

G. Meyer et al, Science, **325**, 1110 (2009)

STM probing of pentacene adsorbed on gold



Joachim et al, PRL, **102**, 176107<sup>3</sup>(2009)

## Perspectives on control

It is also possible to manipulate charge on a single atom



G. Meyer et al, Science, **324**, 1428 (2009)

## anchoring and (logical) addressing distorts/modifies the functionality of the molecule

-mechanical motion that takes place in solution may not be conserved when the molecule is anchored

-field strengths used for electrical/electrochemical addressing distorts the molecule and induces migration.

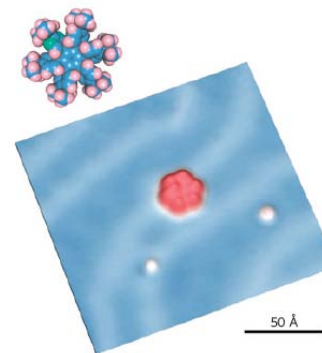
- 
- difficulty of controlling the position (migration), even at low K.
  - difficulty of addressing atoms and molecules with the same atomic precision as for imaging so that they can perform a logic function.

## Position control

### Step-by-step rotation of a molecule-gear mounted on an atomic-scale axis

C. Manzano<sup>1\*</sup>, W.-H. Soe<sup>1\*</sup>, H. S. Wong<sup>1</sup>, F. Ample<sup>2</sup>, A. Gourdon<sup>2</sup>, N. Chandrasekhar<sup>1</sup> and C. Joachim<sup>1,2</sup>

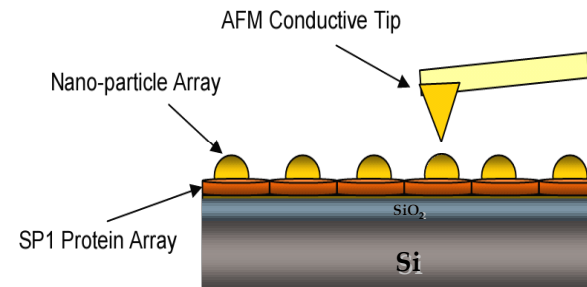
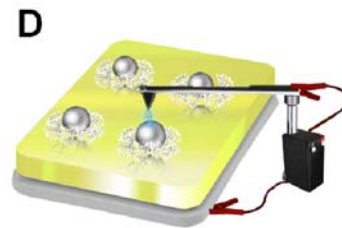
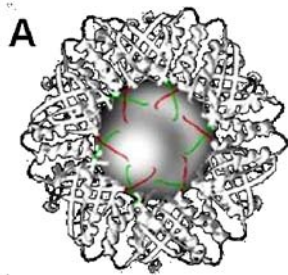
Nature Material, **8**, 576 (2009)



**Figure 1 | HB-NBP molecule.** STM image of a single pinion molecule physisorbed on Au(111); the herringbone reconstruction is clearly seen in the background. The molecule is located in the vicinity of two atomic-scale impurities. One is an atomic-sized defect bound to a herringbone elbow. The other is a gold atom produced after softly indenting the STM tip on the substrate and intentionally moved close to the molecule. The inset at the top left corner shows a space-filling model of the molecule,  $I = 31$  pA,  $V = 100$  mV. A structural formula of the molecule is shown in the Supplementary Information.

One solution explored by MOLOC in collaboration with D. Porath (HUJI) is to trap a larger NP (5 nm) in a ring (SP1) protein that can be immobilized on a surface and form ordered arrays.

➔ Possible to address (charge and discharge) a single hybrid NP.



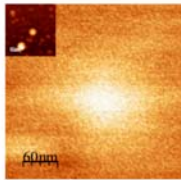
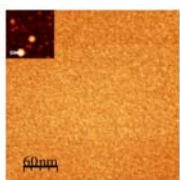
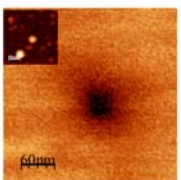
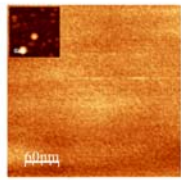
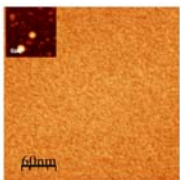
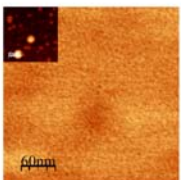
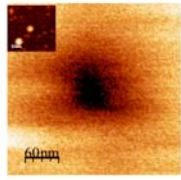
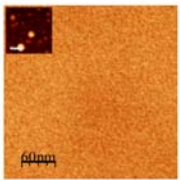
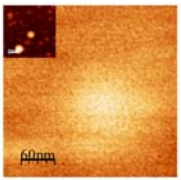
I. Medalsy, M. Klein, A. Heyman, O. Shoseyov, F. Remacle, R. D. Levine and D. Porath, under final revision, 2010.

## Implementation of complex logic operations


- beyond Boolean (Ternary multiplier)
- beyond combinational circuits (FSM).

### AFM tip electrical state

NP charge state

tip \ NP	-1	0	+1
-1			
0			
+1			

output : measured by the tip in EFM mode


 Bright  $\equiv$  repulsion  $\equiv$  +1  
 Neutral  $\equiv$  0  
 Dark  $\equiv$  tip-particle attraction  $\equiv$  -1

- single device, operated at room temperature
- can be extended to more than one digit

# Controlled electrical addressing of a single dopant atom in a FinFET

APPLIED PHYSICS LETTERS 96, 1 (2010)

## 1 Ternary logic implemented on a single dopant atom field effect transistor 2 silicon transistor

3 M. Klein,<sup>2</sup> J. A. Mol,<sup>1</sup> J. Verduijn,<sup>1</sup> G. P. Lansbergen,<sup>1</sup> S. Rogge,<sup>1,a)</sup> R. D. Levine,<sup>2,4,b)</sup> and  
4 F. Remacle<sup>2,3,c)</sup>

5 <sup>1</sup>Kavli Institute of Nanoscience, Delft University of Technology, Lorentzweg 1, 2628 CJ Delft,  
6 The Netherlands

7 <sup>2</sup>The Fritz Haber Research Center for Molecular Dynamics, The Hebrew University of Jerusalem,  
8 Jerusalem 91904, Israel

9 <sup>3</sup>Département de Chimie, B6c, Université de Liège, B4000 Liège, Belgium

10 <sup>4</sup>Department of Chemistry and Biochemistry and Department of Molecular and Medical Pharmacology,  
11 Crump Institute for Molecular Imaging, The University of California Los Angeles, Los Angeles,  
12 California 90095, USA

13 (Received 3 October 2009; accepted 23 December 2009; published online xx xx xxxx)

14 We provide an experimental proof of principle for a ternary multiplier realized in terms of the charge  
15 state of a single dopant atom embedded in a fin field effect transistor (Fin-FET). Robust reading of  
16 the logic output is made possible by using two channels to measure the current flowing through the  
17 device and the transconductance. A read out procedure that allows for voltage gain is proposed.  
18 Long numbers can be multiplied by addressing a sequence of Fin-FET transistors in a row. © 2010  
19 American Institute of Physics. [doi:10.1063/1.3297906]

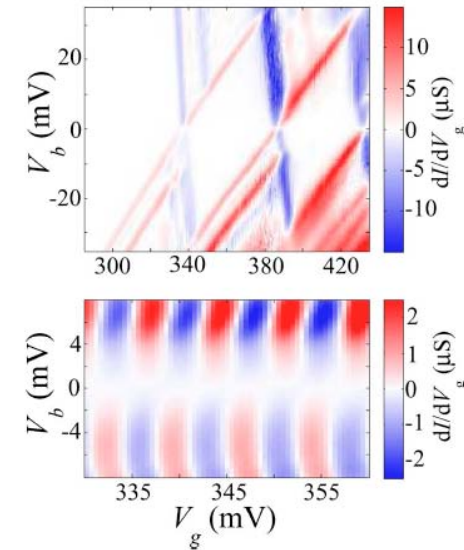
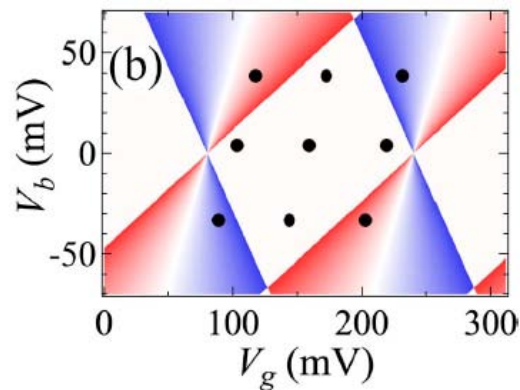
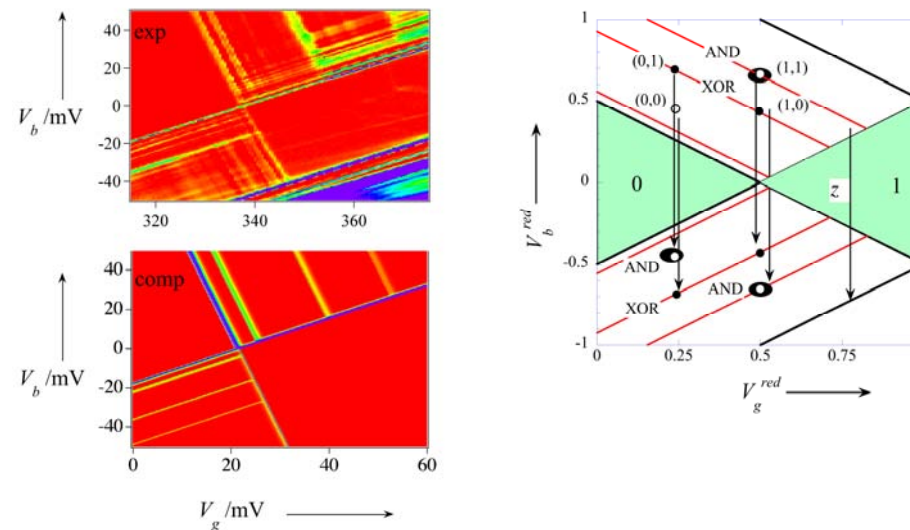
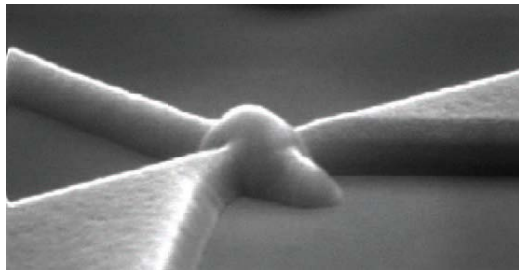


FIG. 2. (Color online) (a) The transconductance,  $dI/dV_g$ , stability diagram shows the transport through a single dopant atom embedded in a Fin-FET device at 1.6 K. The region where transport is Coulomb blocked appears in white. Going from left to right, three stable charge states (+1, 0, -1) of the dopant atom are visible. We use the region of stability of the neutral dopant (middle) to implement the multiplier. The regions of positive and negative  $dI/dV_g$  appear in red and blue, respectively. (b) Transconductance of a many electron SET based on complementary metal-oxide semiconductor technology.

# Controlled addressing of a single dopant atom

## A full adder implementation

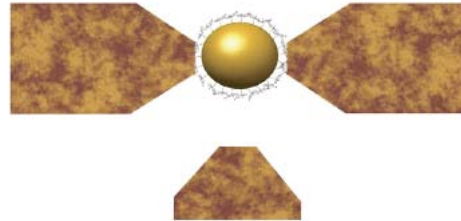
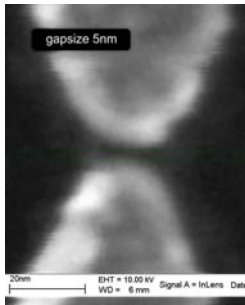


M. Klein, G. P. Lansbergen, J. A. Mol, S. Rogge, R. D. Levine, and F. Remacle, Reconfigurable Logic Devices on a Single Dopant Atom up to a Full Adder by Electrical Spectroscopy, *ChemPhysChem*. **10**: 162-173, 2009.

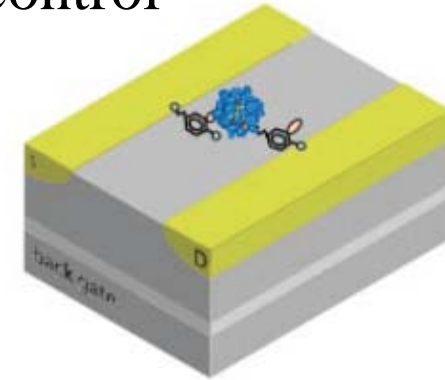
# Perspectives on control of break junctions

Break junctions are also very hard to control

S. Karthäuser (FZ Jülich)



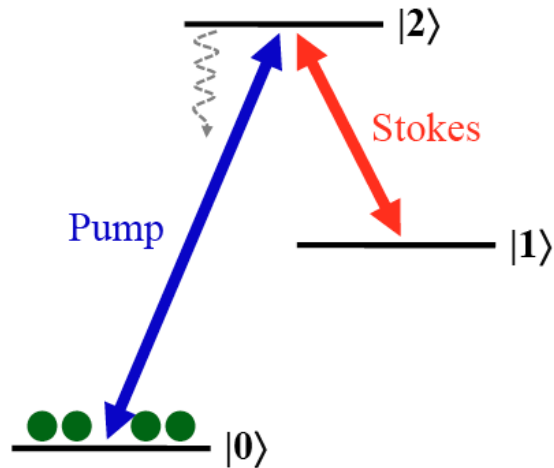
5 nm



- often more than one molecule in the gap if the gap is not small.
- coupling to the electrodes is dynamic, is affected by field strengths
- high applied field strengths distort the molecule (electronic states)
- for very small gaps ( $< 3$  nm), there can be coupling between the two electrodes without a molecule trapped.
- problems for opto/electrical addressing, plasmon of the electrodes.
- vibronic coupling and heat dissipation (probed by SERS, Nature Nano **3**, 2008, 727)

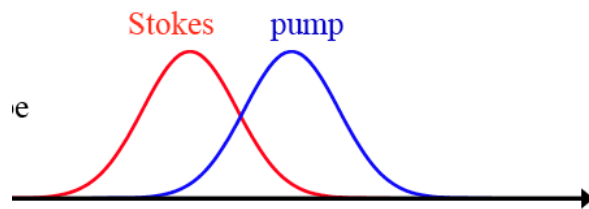
# Optical control of the dynamics of electronic states for implementing logic

Design of a cyclable full adder on a three state system using  
using STIRAP or b-STIRAP coherent addressing,  
FR and R. D. Levine, Phys. Rev. A, 2006, **73**, 0033820



Experimental implementation by  
T. Halfmann (Darmstadt)  
on a rare earth doped solid  
(Pr:YSO)

input

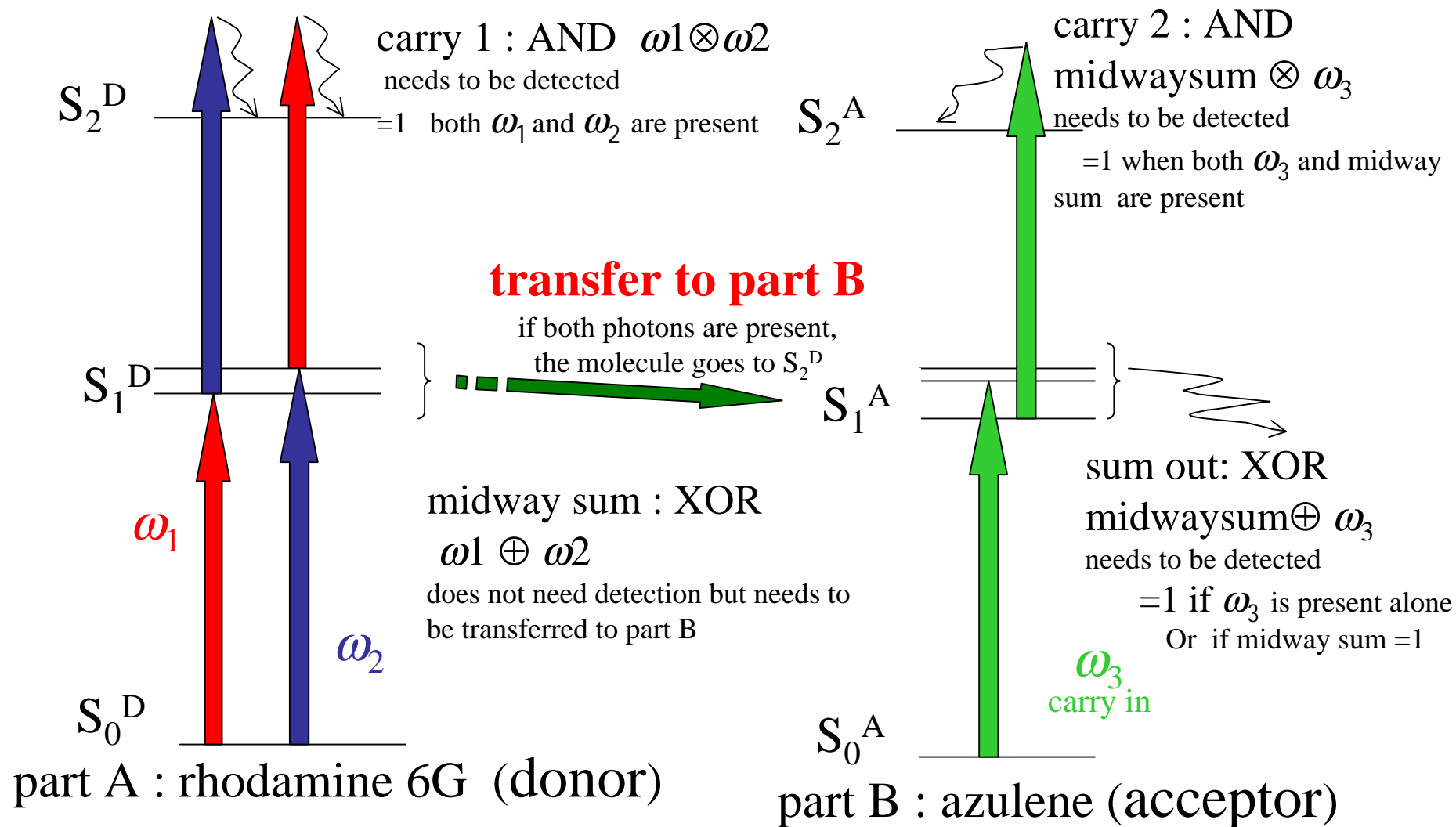


# Cascading and interconnecting molecular devices

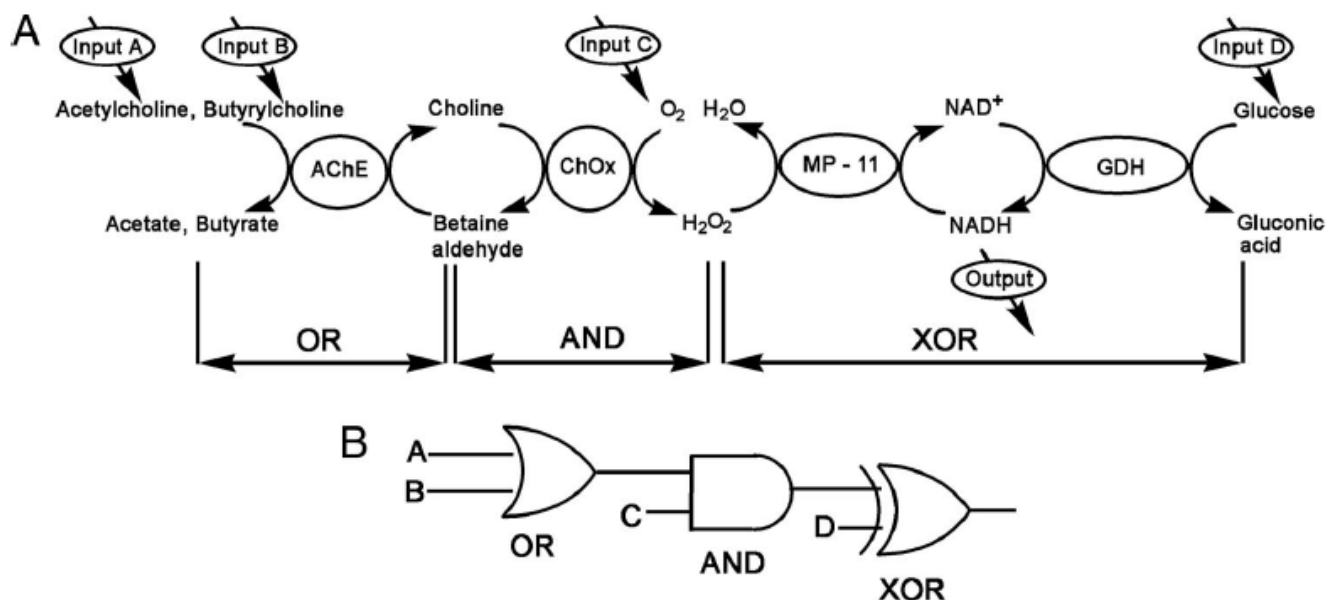
Even harder than control

Challenge is not only to cascade  
but also to cascade more than once!

# concatenation by electronic energy transfer from donor to acceptor in solution



# Cascading more than once in solution by chemical addressing



## Concatenated logic gates using four coupled biocatalysts operating in series

Tamara Niazov, Ronan Baron, Eugenio Katz, Oleg Lioubashevski, and Itamar Willner\*

PNAS, **103**, 17160 (2006)

## Interconnecting molecular devices

- very hard to go beyond more than two units (usually no gain).
- very hard to control when the units are anchored on a surface, or even linked by a molecular bridge.

# New scalable concepts and designs for molecular systems

## Develop a physical theory of computing

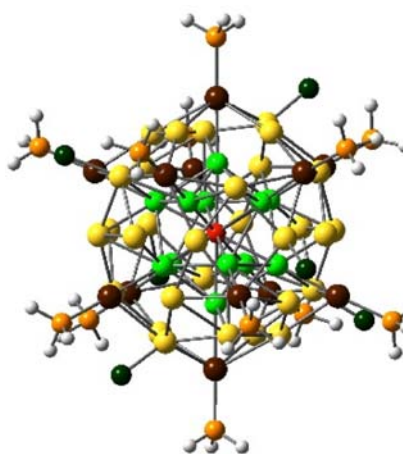
- Beyond the switching paradigm, what is the efficient level of logic complexity to be implemented at the hardware level?
- What are the requirements for the physical system in terms size, internal degrees of freedom?
- Beyond Boolean, what is the right radix, how to relate it to the physical system used for the implementation.
- Beyond combinational circuits :
  - Finite state machines (combinational and memory units)
  - Programmable machines

## Modeling nanoscale systems and their interaction with environment

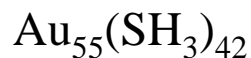
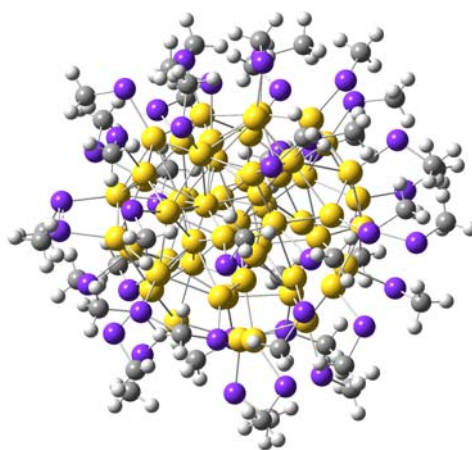
Environment can affect the electronic and functional properties, and  
therefore the logic operation of hybrid nanoscale systems

→ multiscale modeling is necessary (QM/MM)

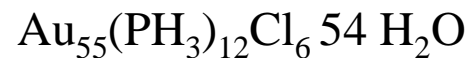
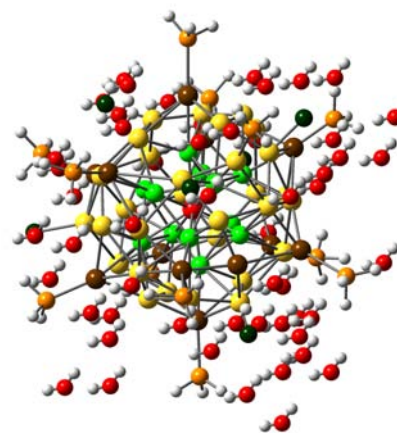
Solvation effect on ligated and functionalized Au<sub>55</sub> nanoparticles



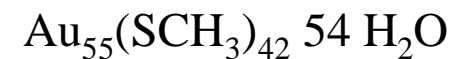
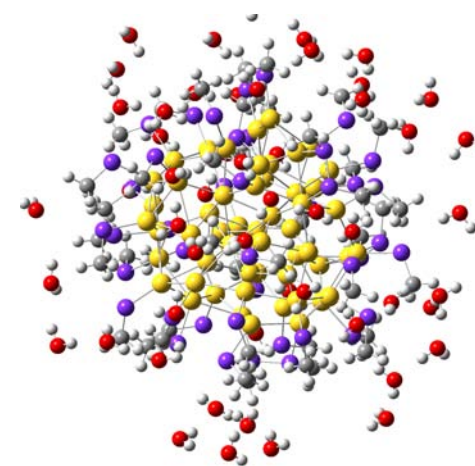
$$U_c = 3.43 \text{ eV}$$



$$U_c = 3.24 \text{ eV}$$



$$U_c = 0.99 \text{ eV}$$

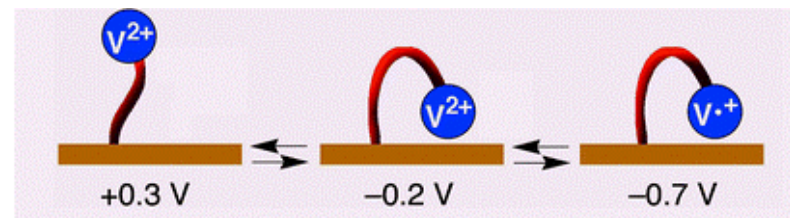
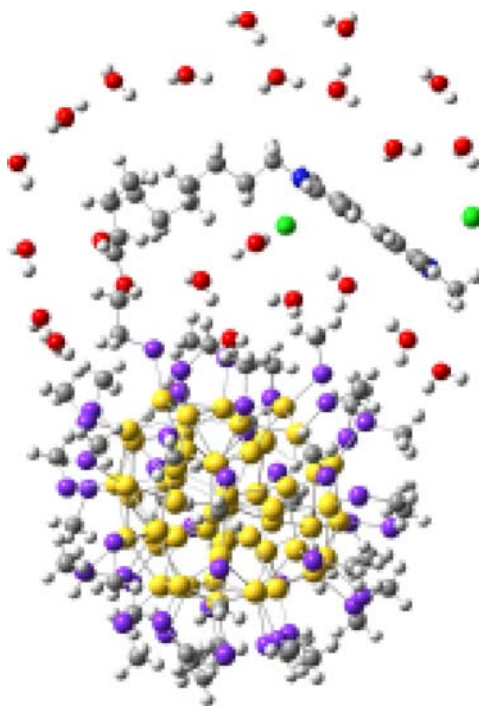
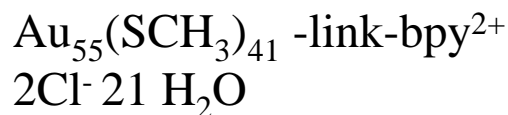
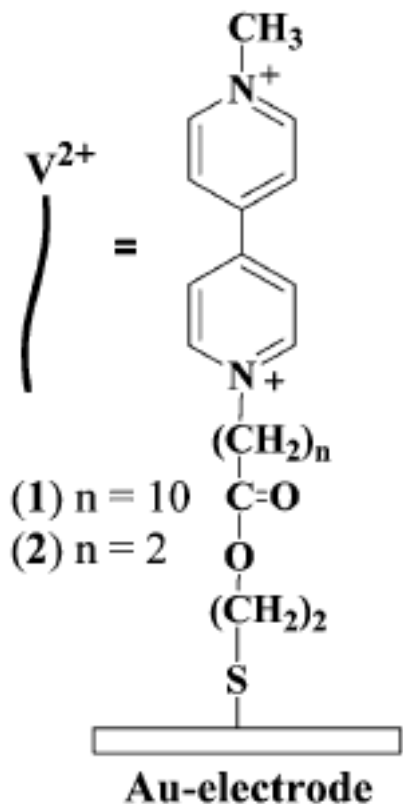


$$U_c = 1.18 \text{ eV}$$

G. Periyasamy and FR, Nanoletters, **9**, 2009 , 3007

G. Periyasamy, E. Durgun, J.Y. Raty, FR, J. Phys. Chem. C submitted

## electrochemical addressing of redox active monolayers or NP



Willner et al, Chem.Comm, 2003, 1542

## electrical addressing



S. Karthäuser, FZ-Jülich, Germany

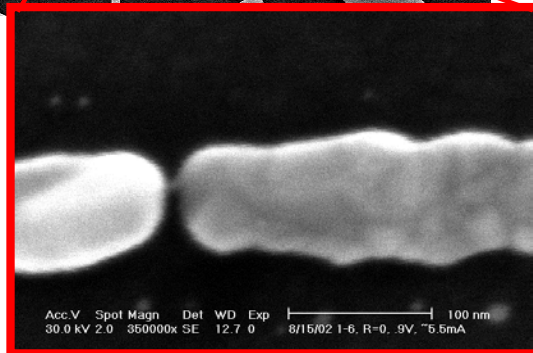
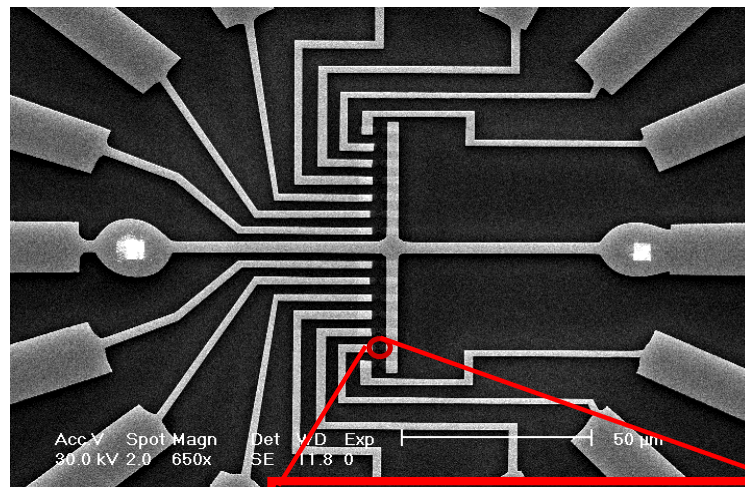
**can be used to implement logic**

Computing the electrochemical response :

G. Periyasamy, R. D. Levine, F. Remacle, Austr. J. Chem. 2010, in press.

# Interfacing Molecular scale devices and systems with the mesoscopic world

Nano and meso scales are hard to interface



Electrical interfacing?  
Optical interfacing?

- Interfacing as late as possible in the logic scheme.
- without losing all the benefit of processing information at the nanoscale.

# Conclusions

- control at the atomic and molecular scale
  - positional
  - addressing and reading
  - control of internal states dynamics
    - as in ‘coherent control’
- interconnection, concatenation
- new scalable concepts and architectures
- interfacing with the mesoscopic world

Thank you for your attention